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SOME ASPECTS ON THE TREATMENT OF SPENT LIQUORS FROM THE CELLULOSE INDUSTRIES IN ORDER TO REDUCE POLLUTION

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Some Aspects on the Treatment of Spent Liquors from the Cellulose Industries in Order to Reduce Pollution.

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1. Pollution effect of pulp mill effluents

In the cellulose industries various kinds of wood are treated in order to separate the cellulose fibers from other constituents of the wood. The main pulping processes are the Kraft (sulfate), the acid sulfite and the neutral sulfite processes. Since the content of cellulose is relatively low, cf. Table 1, about half of the organic matter will remain in the spent liquors from these processes.

Much work has been done to make use of the spent liquors, e.g. for production of ethyl alcohol (1), fodder yeast (1), vanillin (1), and acetic acid (2). However, only a minor part of the organic material can be removed by such processes.

Table 1. Constituents of spruce wood according to Hägglund

cellulose	41.0 %
hemicellulose	26.7 %
lignin	28.6 %
miscellaneous (resin, ash etc)	3.7 %

In may cases the spent liquors are sent directly from pulp washing to sewage, hence polluting lakes and rivers, i.a. by consuming oxygen dissolved in the water when being biologically degraded.

The pollution effect is often measured as the biological oxygen demand (BOD) during a 5 day test (3). The BOD of various types of effluents from pulp washing and bleaching was reported by Bialkowsky and Brown (4), cf. Table 2.

Table 2. BOD of various pulp mill effluents

type of liquor	kg BOD per ton pulp	remarks
acid sulfite	300 - 380	pulp washing
neutral sulfite	120 - 130	
Kraft (sulfate)	390 - 550	
paper sulfite	13 - 17	pulp bleaching
dissolving sulfite	57 - 60	
Kraft (sulfate)	9 - 20	

The values from Table 2 indicate that the untreated waste liquors from a 100,000 ton per year mill (bleached acid sulfite) would cause a BOD of about 100 ton per day. Since the normal BOD of domestic sewages is about 75 g per person and day (3), the pollution equivalent of the pulp mill mentioned would be a city with about 1,300,000 inhabitants. The figures indicate that, in many cases, measures must be taken either to reach sufficiently large recipients, e.g. by building long

sewage pipes, or to decrease the pollution load, e.g. by recovering certain constituents of the spent liquors or by burning them. However, before burning, the spent liquors must be evaporated. Recent investigations (5) show that the BOD of these condensates can not be neglected, cf. Table 3.

Table 3. BOD of various condensates from spent liquor evaporation

type of condensate	kg BOD per m^3	kg BOD per ton pulp
acid sulfite	3 - 10[a]	20 - 60
neutralized acid sulfite	2 - 4	10 - 20
Kraft (sulfate)	1 - 2	6 - 8

a) Lower values apply to soft wood, higher ones to hard wood.

By evaporating and burning, the BOD load can be decreased by 70 - 90 %, depending on the efficiency of the pulp washing. It is, however, necessary to make these processes economically attractive, and this is achieved by recovery of heat and chemicals.

The effective heat value of spent acid sulfite liquors, evaporated to 55 % solids, is about 2000 kcal per kg (6), corresponding to a net saving 2 - 3 Gcal or $3 - 5 per ton pulp. Kraft liquors have somewhat lower, and neutral sulfite liquors considerably lower heat values.

Recovery of chemicals has been applied in Kraft mills for many years, but now the growing use of "soluble" bases, i.e. magnesium, ammonium, and sodium in sulfite mills has necessitated recovery of chemicals also in this branch of the cellulose industry. Table 4 gives an approximate idea of costs for chemicals, if no recovery is applied.

Table 4. Approximate costs for chemicals with various sulfite bases

chemical	$ per ton chemical	$ per ton pulp
CaO (as $CaCO_3$)	10	0.6 - 0.8
MgO (as $MgSO_4$)[b]	30[a]	1.4 - 1.6
NH_3	100	3.6 - 4.4
Na_2O (as NaOH)	75	5.0 - 6.0
Na_2O (as Na_2SO_4)[b]	35[a]	2.4 - 2.9
S	30	3.0 - 3.6

a) corrected for sulfur content
b) possible only in connection with chemical recovery

When burning sulfur containing liquors, one must be aware of the risk of transforming water pollution into air pollution. Flue gases from sulfite liquors may contain up to 0.5 % sulfur dioxide (7), and gases from Kraft liquors up to 0.05 % hydrogen sulfide and mercaptans. Methods of decreasing the air pollution will be briefly discussed below.

2. Treatment of Kraft liquors

In the Kraft process a solution of sodium hydroxide and sulfide is used as the pulping liquor, and hence recovery of the base is necessary. Since the recovery process is well-known and thoroughly described in the literature, it will be only briefly discussed.

The black liquor is separated from the pulp in a system of either filter washers or diffusers, cf. Figure I. A liquor recovery of 95 % may be reached without difficulty. In multi-stage vacuum evaporators the solution is then concentrated from 14 - 20 % to 55 - 60 % solids. In order to fix malodorous volatile sulfur compounds, the black liquor may either be oxidized in a special tower, or the tail gases scrubbed with alkali.

The thick liquor is finally burnt in specially designed boilers. In some cases the flue gases are utilized for final direct evaporation of black liquor. This method seems, however, to cause unnecessary stripping of hydrogen sulfide by the carbon dioxide content of the flue gases. Electric precipitators are normally used for recovery of solids (sodium sulfate) from the gas, and sometimes heat is also recovered in scrubbers of various types.

The green liquor, formed by dissolving the melt from the boiler, is regenerated by clarification, recausticizing with lime, and clarification of the resulting white liquor, which is used for pulping. Nowadays the calcium carbonate sludge is burnt in rotating kilns and reused for causticizing. In this way chemicals are saved and a waste problem solved.

The efficiency of regeneration is 90 - 95 % in the Kraft process, which gives a comparatively low BOD of effluents, i.e. 50 - 70 kg BOD per ton pulp. However, blow gases from digesters and flue gases from boilers contain small percentages of odorous sulfur compounds. Much effort has been taken to eliminate emission to the surroundings, but as yet there seems to be no perfect solution to the problem.

3. Treatment of calcium sulfite liquors

Calcium is the classical base in sulfite pulping, primarily owing to its low price. In most cases, cooking acid is prepared by contacting water, lime stone, and sulfur dioxide in a reaction tower. Recovery of the base has not been regarded as economical, cf. Table 4, but sulfur recovery has been discussed (7).

The spent liquor is very often sent directly to sewage, but is sometimes spread on gravel roads as an anti-dust chemical. References have already been given to processes for utilizing various compounds in the liquors (1, 2).

During the second world war methods were developed for evaporating and burning the liquors, thus recovering heat and decreasing water pollution. The spent liquor is separated from the pulp in a combined blow pit and washing tank. With respect to the lower value of the chemicals, the efficienty is comparatively poor, 75 - 85 %. The solution is then evaporated from 10 - 15 to about 55 % solids in multistage evaporators of either vacuum or back-pressure type. In this case acid resistant steel must be used in heat exchangers, expansion vessels, etc. Another cost increasing factor is the scaling of calcium sulfate, which necessitates arrangements for channel switching or other cleaning (e.g. condensate washing) of heating surfaces (6).

The calcium sulfite thick liquor is then burnt in a boiler, which must be specially equipped, e.g. with a Loddby furnace, in order to facilitate the ignition of the liquor. The inorganic residue is taken up in cyclones as ash, containing mainly calcium sulfate, oxide and carbonate. It is normally wasted, but in some cases it is used for neutralizing sulfite liquor prior to fermentation.

The BOD of effluents from a sulfite mill using spent liquor burning may reach 60 - 180 kg per ton pulp, depending on the efficiency of pulp washing, type of pulp etc. The flue gas from calcium liquor burning holds 0.3 - 0.5 % sulfur

dioxide and some fly ash. No injuries to surrounding vegetation have been reported so far.

4. Treatment of magnesium sulfite liquors

Magnesium has met a renaissance as base in sulfite pulping in the last ten years. As a metter of fact, the first Swedish sulfite mill started with magnesium in 1874, but then changed over to calcium. Now the interest bas been directed towards magnesium in the search for bases with higher solubility than calcium (magnesium permits operation at pH up to 5.5 - 6.0). Several new sulfite mills have been equipped for magnesium pulping, e.g. Cosmopolis (Wash., USA), started in 1957, Sitka (Alaska, USA) in 1960, and Nymölla (Sweden) in 1962.

Table 4 shows that magnesium salts are rather cheap, and the base is in some cases used without recovery of chemicals (e.g. at Wausau, Wisc., USA, and Hunsfos, Norway). Normally the magnesium mills are, however, equipped with recovery units operating according to the flow sheet in Figure II.

The cooking acid is prepared by dissolving sulfur dioxide in a slurry of magnesium oxide (8). The recovered spent liquor is evaporated just as calcium liquor, and burnt in a specially designed boiler. In this case the inorganic substance is almost completely dissociated into sulfur dioxide and magnesium oxide. The ash is first collected in cyclones, and then washed with water to a slurry, which is used for absorption of sulfur dioxide from the flue gases in a tray of absorption towers.

5. Treatment of ammonium sulfite liquors

Ammonium is a soluble base, which is easy to handle but rather expensive, cf. Table 4. In some old mills it is used instead of calcium in order to increase the pulping capacity or give a higher degree of freedom in the choice of pulp wood (e.g. at Lebanon, Ore., USA, and Toten, Norway). However, economical recovery of the base is not possible; only sulfur may be reclaimed.

After separation from the pulp, the spent liquor is evaporated and burnt. During evaporation a tendency to formation of condensation products has been observed, sometimes interfering with the operation and necessetating cleaning with nitric acid. The boiler normally operates very smoothly, since only gaseous products are formed: the inorganic compounds are oxidized to nitrogen oxide and sulfur dioxide.

6. Treatment of sodium sulfite liquors

Many processes have been suggested for the recovery of the sodium base. The reason is that sodium gives a total freedom in choosing pH of pulping, but is too expensive for being used without recovery, cf. Table 4. In several cases "cross recovery" has been applied, i.e. fresh chemicals are added to the sulfite mill, and the spent liquors transferred to a neighbouring Kraft mill. The draw-back is that the sulfite capacity may reach only a certain fraction of the Kraft capacity.

Among the separate recovery systems, the Stora Kopparberg process (8) is in widest use (Skutskär and Domsjö, Sweden, and Nova Scotia, Canada). The features of this system are shown in Figure III. The recovered spent liquor is concentrated in acid resistant evaporators and burnt in a special boiler equipped with electric precipitators to collect ash. The inorganic chemicals are obtained as

a melt of sodium sulfide (75 %) and carbonate, which is dissolved and clarified. The solution is then carbonated, and the sulfur content stripped off as hydrogen sulfide, which is contacted with sulfur dioxide in a Claus reactor and transformed to elemental sulfur.

The bicarbonate solution is mixed with bisulfite under formation of carbon dioxide and sulfite, which is used for sulfur dioxide absorption and cooking liquor preparation. In the sulfur system the roast gases are washed first with water used for preparation of liquid sulfur dioxide, and then with sulfite solution. Finally the flue gases, containing 0.3 - 0.4 % sulfur dioxide, are also scrubbed with sulfite solution. The Stora process may seem rather complicated, but since only liquid and gaseous streams are handled, the operation is smooth.

The Sivola process (8) is practiced at Rauma (Finland) and its principal features are much the same as in the Stora process. The clarified green liquor is, however, partly carbonated with carbon dioxide from flue gases. Bicarbonate crystals are then separated on a filter and used for preparatic of sulfite-bisulfite solution for the first cooking stage. The mother liquor is utilized in a third cooking stage, which is typical to the process. Liquid sulfur dioxide for the second stage is prepared by stripping cooking liquors and by condensing the gas, at high pressure.

Another process using a Kraft boiler and sulfide recirculation is the Western-Precipitation process (8), tested i.a. at Nekoosa (Wisc., USA).

Recent investigations have shown that it is theoretically possible to direct the combustion of spent sodium liquor so that a solid phase of carbonate is obtained, and the sulfur is completely volatilized as sulfur dioxide. This process is under development in Canada (Gauvin's AST-process) (8) and Sweden. Since an entirely new technique must be applied, many problems concerning materials of construction, temperature control, etc. have to be solved before the process can be utilized on a full scale.

7. Treatment of neutral sulfite semi-chemical liquors

Also in semi-chemical pulping "cross recovery" has been applied in several cases. Since cooking liquors of lower purity can be accepted, recovery systems have been developed, which are less complicated than in the acid sulfite process.

In the Mead recovery process (8), used i.a. at Watervliet (Mich., USA), carbon dioxide from flue gases are utilized for the whole green liquor carbonation and therefore a comparatively high thiosulfate content is obtained. The solution is then sulfited with sulfur dioxide in the flue gases and used as pulping liquor.

The Zimmermann process (8), employed by Borregaard in Norway, is based on wet combustion of the spent liquors, cf. Figure IV. These are first neutralized with carbonate and then oxidized with air at 200-300°C and 50-200 atm. A turbine operated by expanding gases, is used for the air compression. The sodium sulfate is finally converted to carbonate by barium salts circulating in the system, and sulfited by sulfur dioxide from the barium cycle.

8. BOD development at a Swedish pulp mill

The effect of various measures to decrease pollution is illustrated by Figure V, showing the development of BOD of wasted liquors at a Swedish sulfite mill. The BOD was first decreased to about 75 % by removing sugar from the liquor by

fermentation, then to about 35 % by evaporating and burning the calcium sulfite liquor. Finally the improved pulp washing connected with switching over to sodium base further decreased the output so that the BOD is presently not higher than in 1932.

Air pollution increased when the liquor burning started, then decreased at the base switching, and will be practically eliminated by a flue gas scrubber, which will be in operation in 1963.

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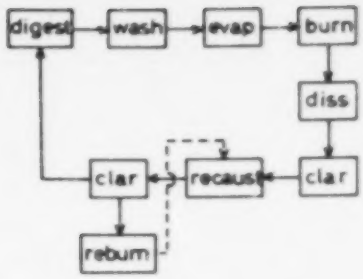

Figure I. The Kraft process.

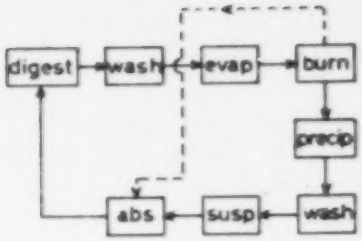

Figure II. The Mg sulfite process.

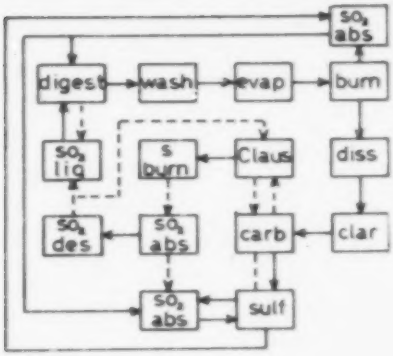

Figure III. The Stora process.

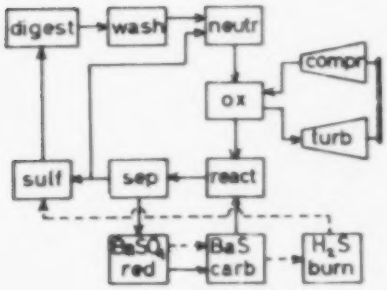

Figure IV. The Zimmermann process.

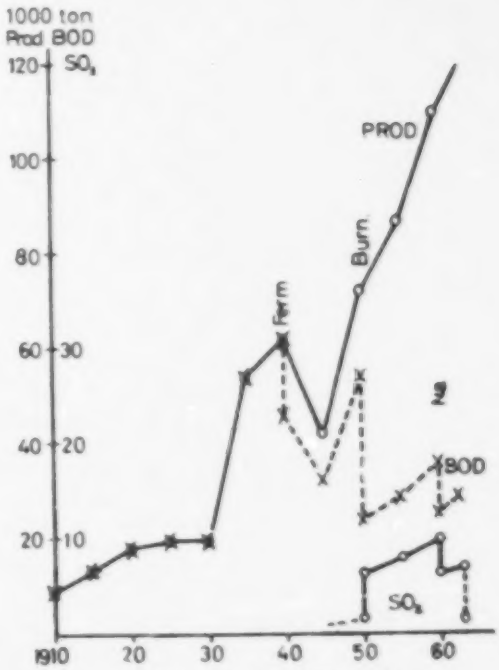

Figure V BOD at a Swedish mill.

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